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Synthesis and characterization of novel fluorinated polyimides derived from 1,1′-bis(4-aminophenyl)-1-(3-trifluoromethylphenyl)-2,2,2-trifluoroethane and aromatic dianhydrides

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Abstract

A novel fluorinated aromatic diamine 1,1′-bis(4-aminophenyl)-1-(3-trifluoromethylphenyl)-2,2,2-trifluoroethane (6FDAM) was synthesized in a simple procedure, which was then employed to prepare a series of fluorinated polyimides with commercial aromatic dianhydrides, such as pyromellitic dianhydride (PMDA), 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane (6FDA), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4′-oxydiphthalic anhydride (ODPA). The polyimides exhibited good solubility in strong dipolar solvents such as NMP, DMAc, DMF and *m*-cresol as well as some of low boiling point organic solvents of THF and $CHCl_3$, etc. Experimental results indicated the polyimides possessed low moisture adsorptions of 0.42–0.95%, low dielectric constant of 2.71–2.95 at 1 MHz, high dielectric strength of 92.0–122.6 kV/mm and good optical transparency with cutoff wavelengths of UV–vis at 330–375 nm. The polyimides also exhibited good mechanical properties as well as excellent thermal and thermo-oxidative stability. The fluorinated polyimides possessed better solubility, lower dielectric constant and water adsorption as well as higher optical transparency than the representative non-fluorinated polyimide derived from PMDA and 4,4′-oxydianiline (ODA).

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Keywords: Fluorinated polyimides; Solubility; Thermal stability; Dielectric properties

1. Introduction

Polyimide materials have been widely used in microelectronic devices such as inter-lay dielectrics passivation layer in multi-layer structures, the substrate of flexible printed circuit boards, stress-relief layers in high-density electronic packaging due to their excellent mechanical, thermal, electrical properties [1–5]. However, conventional polyimide materials possess bad solubility, high moisture adsorption and relatively high dielectric constant, which limit their availability in microelectronic industry. With the development of microelectronic

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industry polyimides employed in these fields should possess following excellent combined properties: easy processing and low curing temperature, moisture resistance, low dielectric constant and dissipation factor, high dielectric strength and high optical transparency. The introduction of fluorine-containing groups in backbone or side chain of the polymer leading to great benefits for improving polymer solubility as well as electrical and dielectric performance, is an efficient method to meet the above-mentioned demands. That arises from the special characteristics of fluorine, such as low polarizability, small dipole, hydrophobicity and oxidization-resistance as well as relative larger free volume [6]. Therefore, many novel fluorinated polyimides have been prepared [7–11]. Additionally, polyimides with high insulating properties are also desirable in high frequency electrical devices [12–15].

In this article, a novel fluorinated aromatic diamine 1,1′-bis(4-aminophenyl)-1-(3-trifluoromethylphenyl)-2,2,2-trifluoroethane (6FDAM) was successfully synthesized by the coupling reaction of 3′-trifluoromethyl-2,2,2-trifluoroacetophenone with aniline hydrochloride in a convenient procedure. A series of fluorinated polyimides based on 6FDAM and various aromatic dianhydrides were prepared in a two-step chemical imidization. As comparison, the representative non-fluorinated polyimide derived from 4,4′-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) was synthesized from a two-step thermal imidization. The solubility, thermal and thermo-oxidative stability, mechanical properties, electrical and dielectric properties as well as optical transparency were investigated.

2. Experimental

2.1. Materials

Aniline hydrochloride, aniline and 4,4′-oxydianiline (ODA) (Beijing Beihua Fine Chemicals Co., China) were used as received. Dianhydrides of pyromellitic dianhydride (PMDA) (Across chemicals Co.), 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane (6FDA) (Hoechst Co. Germany), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) (Across chemicals Co.) and 4,4′-oxydiphthalic anhydride (ODPA) (Across chemicals Co.) were dried for 6 h at 160 °C in vacuum prior to use. 1-Methyl-2-pyrrolidinone (NMP) was distilled in vacuum from P_2O_5 and stored in a sealed flask.

2.2. Measurements

^{1}H NMR and ^{13}C NMR spectra were measured with a Varian Unity 300 spectrometer, using $CDCl_3$ or DMSO-d_6 as solvent. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin–Elmer 782 Fourier transform spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed using a Perkin–Elmer TGA-7 thermo gravimetric analyzer in nitrogen at a heating rate of 10 °C/min. Intrinsic viscosity of polyimides in NMP solution was measured at 25 °C with Ubbelohde viscometer. Measurement of molecular weights and molecular weight distributions were carried out on Showa Denko GPC-101 with DMF as the eluent. Mechanical properties were measured on Instron 8810 tensile machine with 0.60 cm wide specimens in accordance with GB 1447-83 at a rate of 5.0 mm min^{-1}. The water adsorptions were determined by weighing the changes of a specimen before and after immersing in boiling water for 30 min. Dielectric properties were performed by the bridge method with a LKI-1 capacitance meter at a frequency of 1 MHz and 25 °C. Insulating properties were measured with a KZT (X) high-voltage control equipment. Ultraviolet–visible (UV–vis) spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature.

2.3. Monomer synthesis

2.3.1. 3′-Trifluorometheyl-2,2,2-trifluroacetophenone (6FAPO)

6FAPO was synthesized according to the method we previously reported [16]. B.p.: 153.5 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 8.38 (s, 1H), 8.23–8.27 (d, 1H), 7.92–7.98 (d, 1H), 7.65–7.78 (t, 1H). MS (EI, m/e, % relative intensity): 242 (M^+, 10.2). Elemental analysis: calcd for $C_9H_4F_6O$: C, 44.65; H, 1.67; found: C, 44.62; H, 1.64.

2.3.2. 1,1′-Bis(4-aminophenyl)-1-(3-trifluoromethylphenyl)-2,2,2-trifluoroethane (6FDAM)

A mixture of 6FAPO (20.000 g, 0.08 mol), aniline hydrochloride (20.000 g, 0.16 mol) and aniline (80 mL) was heated at reflux for 24 h. Then sodium bicarbonate (20.000 g) was added and the mixture was steam distilled until the distillate was clear. The solid residue was dissolved in a mixture of 100 mL hydrochloride and 400 ml water, to which

20% ammonia was added dropwise until the mixture became neutral. The precipitate was filtrated and washed with water for several times and then dried at 110 °C for 6 h in vacuum, followed by recrystallization from methanol to give a gray solid. Yield: 28.00 g, 85.4%. M.p.: 124.1 °C.^{1}H NMR ($CDCl_3$, δ ppm): 7.58–7.61 (d, 1H), 7.48 (s, 1H), 7.36–7.45 (m, 2H), 6.82–6.90 (d, 4H), 6.58–6.73 (d, 4H), 3.34 (s, 4H). ^{13}C NMR ($CDCl_3$, δ ppm): 147.5, 146.8, 143.2, 142.1, 133.9, 131.8, 131.0, 130.5, 130.4, 130.2, 128.9,128.0, 127.5, 127.3, 127.2, 126.9, 124.5, 115.1. FT-IR (KBr, cm^{-1}): 3468, 3440, 3347, 3227, 1626, 1517, 1431, 1326, 1262, 1165, 1125, 829, 801, 758. MS (EI, *m*/*e*, % relative intensity): 410 (M^+, 23.2). Elemental analysis: calcd for $C_{21}H_{16}F_6N_2$: C, 61.46; H, 3.93; N, 6.83; found: C, 61.43; H, 3.89; N, 6.78.

2.4. Polymer synthesis

In a typical experiment, PI-3 (BTDA/6FDAM) as an example, 6FDAM (1.642 g, 4.0 mmol) was dissolved in 16 mL of NMP in a 100-mL three-necked flask fitted with a nitrogen inlet pipet and a mechanical stirrer, to which the aromatic dianhydride BTDA (1.289 g, 4.0 mmol) was added with stirring. The mixture was stirred at room temperature in nitrogen for 24 h to yield a poly(amic acid) (PAA) solution with 15 wt.% solid content. A mixture of acetic anhydride and pyridine (6:4, v/v) was added into the above-mentioned PAA solution and stirred at the ambient temperature for 2 h, and 60 °C for 4 h. Then the homogeneous polyimide solution was poured into methanol and the precipitate was collected by filtration, washed with methanol, and dried at 120 °C in vacuum to give a yellow polyimide (PI-3) with the yield of 94%. ^{1}H NMR ($CDCl_3$, δ ppm): 8.09–8.31 (m, 6H), 7.80–7.89 (d, 1H), 7.74 (s, 1H), 7.42–7.53 (d, 4H), 7.31–7.39 (m, 2H), 7.10–7.21 (d, 4H). FT-IR (KBr, cm^{-1}): 3072, 1783, 1728, 1613, 1515, 1374, 1329, 1224, 1156, 1090, 858, 716. Elemental analysis: calcd for $C_{38}H_{18}F_6N_2O_5$: C, 65.52; H, 2.60; N, 4.02. Found: C, 65.66; H, 2.69; N, 3.88.

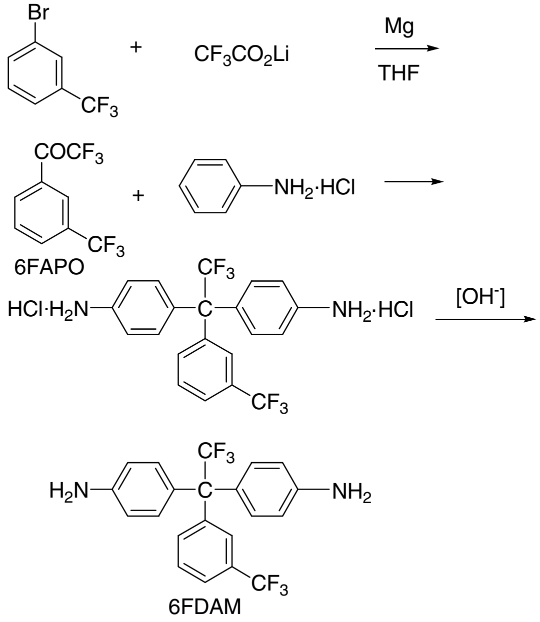
PI-1 (PMDA/6FDAM), PI-2 (6FDA/6FDAM) and PI-4 (ODPA/6FDAM) were prepared in the same procedures as PI-3 by polymerization of 1 equiv. of 6FDAM and 1 equiv. of PMDA, 6FDA and ODPA, respectively at 15% solid content in NMP. As comparison, the non-fluorinated polyimide PI-5 derived from PMDA and ODA was prepared in a two-step thermal imidization as followings.

ODA (8.009 g, 40 mmol) was dissolved in 150 mL of NMP in a 300 mL flask equipped with a nitrogen inlet pipet and a mechanical stirrer. PMDA (8.720 g, 40 mmol) was added to the solution and the mixture was stirred at room temperature for 6 h under nitrogen to give a homogeneous and viscous PAA solution, which was then cast on a clean glass plate, followed by heating in an oven with a programmed procedure: 80 °C/1 h, 120 °C/1 h, 180 °C/1 h, 250 °C/2 h, and 300 °C/1 h, successively. The polyimide film of PI-5 was obtained after peeling off the glass plate.

3. Results and discussion

3.1. Monomer synthesis

Diamine 6FDAM was synthesized according to the process as shown in Scheme 1. First 6FAPO was prepared with the method we previously reported, which was then used to react with aniline hydrochloride by coupling to afford a diamine hydrochloride. The diamine hydrochloride was released with aqueous ammonium hydroxide to give the novel diamine 6FDAM. Further purification was performed by recrystallization. The facile synthetic procedure enables the preparation of 6FDAM in large scale implying a potential availability in



Scheme 1. Synthesis of the fluorinated diamine 6FDAM.

microelectronic industry. The diamine 6FDAM was found stable without any color change in air after three months due to the fluorine-containing structure in the both main and side chain. This feature was different with common non-fluorinated diamines which were easy to be oxidized and became black in air, implying the good storage capability. The structure of 6FDAM was identified by FT-IR, ^{1}H NMR, ^{13}C NMR, MS spectra and elemental analysis in great agreement (see Fig. 1).

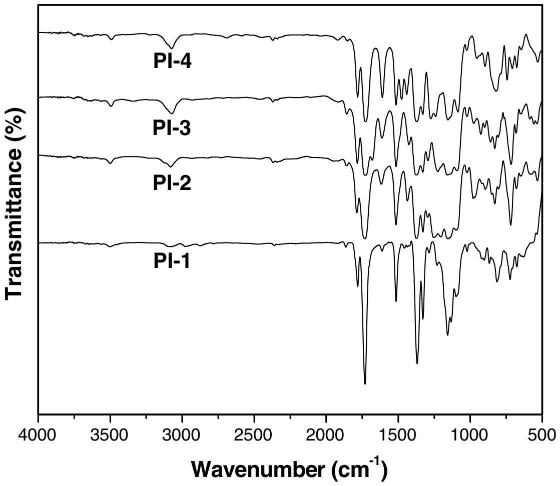


Fig. 2. FT-IR spectra of the fluorinated polyimides.

3.2. Polymer synthesis

The fluorinated polyimides were prepared from 6FDAM and various aromatic dianhydrides by a two-step chemical polymerization procedure. 6FDAM reacted with dianhydrides in NMP to give PAA solutions, which were then chemically imidized by the mixture of acetic anhydride and pyridine to yield the polyimides. A series of fluorinated polyimides, PI-1, PI-2, PI-3 and PI-4 were synthesized by the polymerization of 1 equiv. of 6FDAM and 1 equiv. of aromatic dianhydrides, including PMDA, 6FDA, BTDA and ODPA at 15% solid content in NMP, respectively. Non-fluorinated PI-5 derived from PMDA and ODA was synthesized as comparison in a well known two-step thermal imidization instead of the chemical one due to its low solubility. Fig. 2 compared FT-IR spectra of the fluorinated polyimides, in which the imide I band at 1783 cm^{-1} (C=O asymmetrical stretching), imide II band at ~1728 cm^{-1} (C=O symmetrical stretching), imide III band at ~1090 cm^{-1}, and imide IV band at ~716 cm^{-1} (imide ring bending vibration) can be observed clearly. In addition, the absorption peak around 3500 cm^{-1} originated from the N–H asymmetrical stretching vibration and the peak at ~1374 cm^{-1} for C–N stretching were also found (see Scheme 2).

Fig. 3 depicted the ^{1}H NMR spectrum of PI-3 derived from 6FDAM and BTDA, in which all the protons were clearly assigned in good agreement with its structure. The characterization by ^{1}H NMR, FT-IR and elemental analysis confirmed that all the polymers have the expected chemical structures.

Table 1 listed the physical properties of the fluorinated polyimides. The fluorinated polyimides, with colors from white to yellow, were prepared in high yields of 92–95%. The inherent viscosity of polyimides ranged in 0.45–0.62 dl/g in NMP at 25 °C, indicating that the polymers with relatively high molecular weights were obtained, that was further confirmed by gel permeation chromatography (GPC) measurements. The fluorinated polyimides exhibited M_w and polydispersities (M_w/M_n) in the range of 135 200–223 400 and 1.29–1.45, respectively.

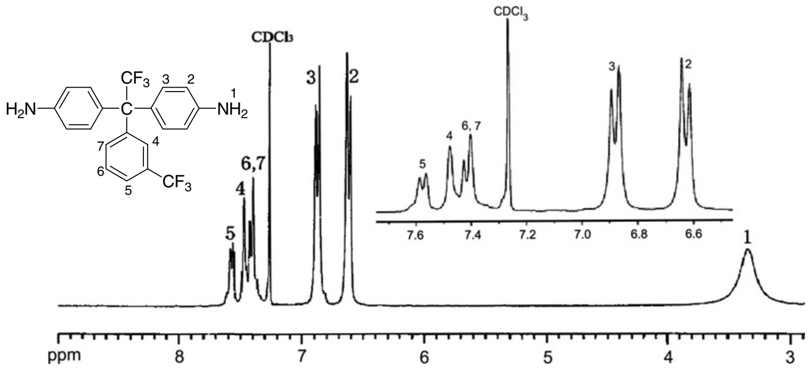
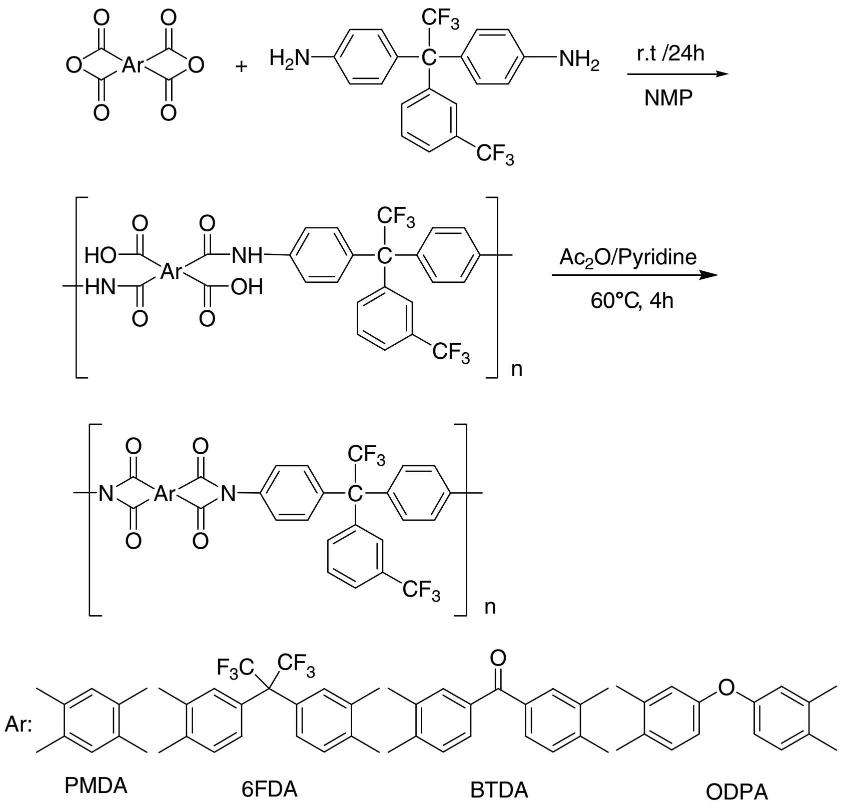


Fig. 1. ^{1}H NMR (CDCl$_3$, 300 MHz) spectrum of 6FDAM.



Scheme 2. Synthesis of the fluorinated polyimides.

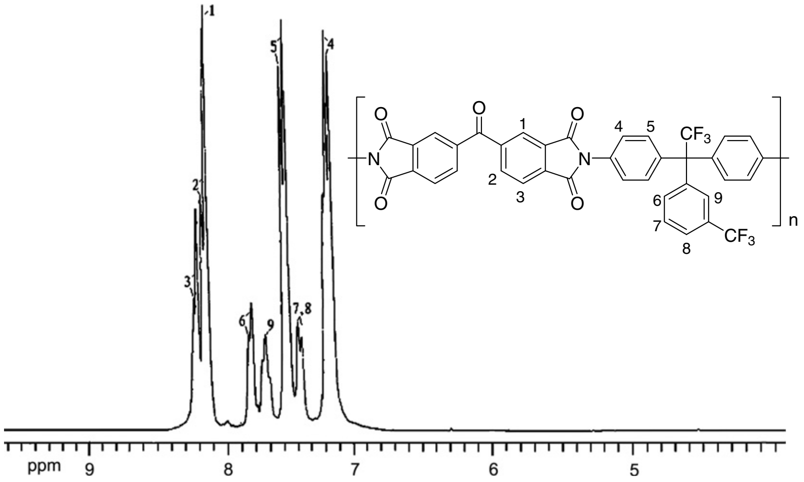


Fig. 3. ^{1}H NMR (DMSO-d_6, 300 MHz) spectrum of PI-3.

3.3. Polymer solubility

The fluorinated polyimides could readily dissolved in many organic solvents to afford homogeneous polymer solution. The solubility of the polyimides was qualitatively determined by dissolving 0.5 g of polyimide in 9.5 g of solvent (5 wt.% of solid content) at room temperature. The solubility of the fluorinated polyimides was summarized in Table 2, from which it was found all the polyimides

Table 1
Physical properties and elemental analysis of the polyimides[a]

PI	Yield (%)	Color	η_{inh}[a] (dL/g)	M_w[b] (GPC)	M_w/M_n	Formula	Elemental analysis (%)			
							Calcd.	C	H	N
							Found			
PI-1	92	Yellow	0.62	223400	1.31	$C_{31}H_{14}F_6N_2O_4$	Calcd.	62.85	2.38	4.73
							Found	62.32	2.35	4.75
PI-2	95	White	0.45	135200	1.45	$C_{40}H_{18}F_{12}N_2O_4$	Calcd.	58.69	2.22	3.42
							Found	58.88	2.35	3.59
PI-3	94	Yellow	0.61	190500	1.29	$C_{38}H_{18}F_6N_2O_5$	Calcd.	65.52	2.60	4.02
							Found	65.66	2.69	3.88
PI-4	93	Yellow	0.51	167500	1.34	$C_{37}H_{18}F_6N_2O_5$	Calcd.	64.92	2.65	4.09
							Found	65.39	2.87	4.24

[a] η_{inh}: inherent viscosity determined in NMP at 25 °C.
[b] Measured using DMF as eluent.

Table 2
Solubility of the polyimides at room temperature[a]

Solvents	PI-1	PI-2	PI-3	PI-4	PI-5
NMP	++	++	++	++	−−
DMSO	++	++	++	++	−−
DMAC	++	++	++	++	−−
DMF	++	++	++	++	−−
m-cresol	++	++	++	++	−−
THF	+−	++	+	++	−−
$CHCl_3$	+−	++	+	+	−−
Acetone	+−	++	+−	+	−−
Methanol	−−	−−	−−	−−	−−

[a] ++: easy to dissolve at room temperature in 24 h; +: soluble after a long time over 24 h; +−: partially soluble; −−: insoluble.

were soluble in strong dipolar solvents such as NMP, DMAc, DMF and *m*-cresol. For low boiling point organic solvents, PI-2, PI-3 and PI-4 were soluble in $CHCl_3$ and THF, whereas PI-1 derived from 6FDAM and PMDA was partially soluble in these solvents owning to the rigid structure. PI-2 with the highest fluorine content derived from 6FDAM and 6FDA showed the best solubility implying the incorporation of fluorinated groups could efficiently improve the solubility. The excellent solubility of the fluorinated aromatic polyimides could be explained by the effect of the unsymmetrical trifluoromethylphenyl structure in the polymer backbone as well as high loadings of fluorine, which resulted in the decrease of the interaction of polymer chain by increasing the distance of the polymer–polymer chains.

Recently, advanced microelectronic packaging technology such as Surface Mount Technology (SMT) need to expose the devices at a soldering temperature of 220–250 °C, which demands the packaging materials can be processed around 200 °C. The good solubility of these fluorinated polyimides in low boiling point solvents enables the preparation of coatings or thin films at a relatively low temperature, which was desirable feature for the advanced microelectronic packaging.

3.4. Thermal properties

Thermal behaviors of the fluorinated polyimides were evaluated by TGA (Fig. 4) and DSC (Fig. 5) as summarized in Table 3. All the polyimides showed a similar TGA curves with decomposition temperatures ranged in 524–569 °C in nitrogen atmosphere. The polyimides did not show obvious

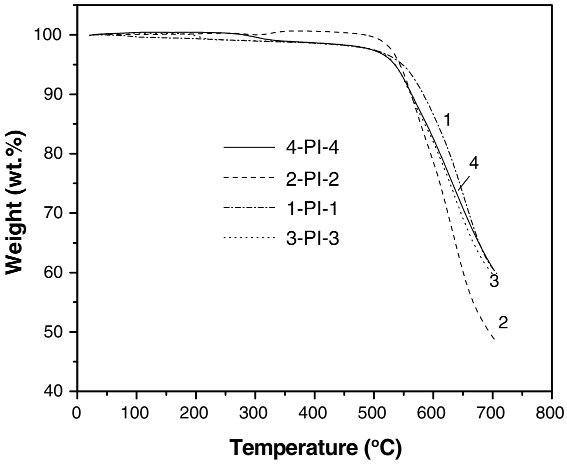


Fig. 4. TGA curves of the polyimides (in nitrogen at a heating rate of 10 °C/min).

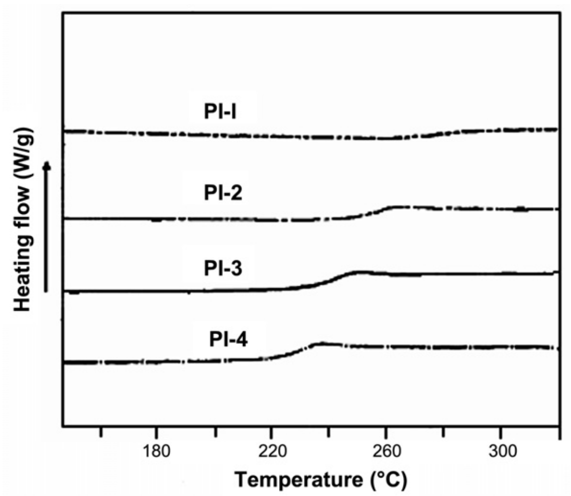


Fig. 5. DSC curves of the polyimides.

Table 3
Thermal properties of the fluorinated polyamides[a]

Polyimide	PI-1	PI-2	PI-3	PI-4
T_g (°C)	282	261	238	242
T_d (°C)	569	530	524	526
T_5 (°C)	547	543	535	536
T_{10} (°C)	583	562	563	562

[a] T_d: onset decomposition temperature; T_5, T_{10}: the decomposition temperatures at 5% and 10% weight loss, respectively.

weight loss before the scanning temperature reached upon to 500 °C in nitrogen, indicating that no thermal decomposition occurred. The temperatures at 5% of weight loss were in the range of 535–547 °C. A relative order of decomposition temperature was PI-1 > PI-2 > PI-4 > PI-3, in which PI-2 (530 °C) with the highest fluorine loading shows slightly higher decomposition temperature than PI-3 (524 °C) and PI-4 (526 °C), implying that the incorporation of fluorinated group would not decreases the thermal stability of polymers. Fig. 5 showed the DSC curves in which the glass transition temperatures (T_g) was in the range of 238–282 °C. PI-1 derived from 6FDAM and PMDA exhibited the highest T_g value (282 °C) probably due to its most rigid structure as compared with other polyimides, while PI-3 showed the lowest T_g of 238 °C for its flexible polymer chain. Fig. 6 depicted the thermal and thermo-oxidative stability of polyimides isothermal aging at 350 °C in nitrogen and air atmosphere. After 120 h isothermal aging in nitrogen, the weight loss in nitrogen increased in the order of PI-4 (4.2%) < PI-2 (5.7%) < PI-1 (6.6%) < PI-3 (7.9%), while in air flowing atmosphere the order is PI-2 (6.4%) < PI-4 (7.5%) < PI-3 (8.0%) < PI-1 (10.5%). It was observed that the PI-2 showed the best thermo-oxidative stability in air due to the introduction of oxidization-resistant CF_3 groups in the polymer backbone and side chains.

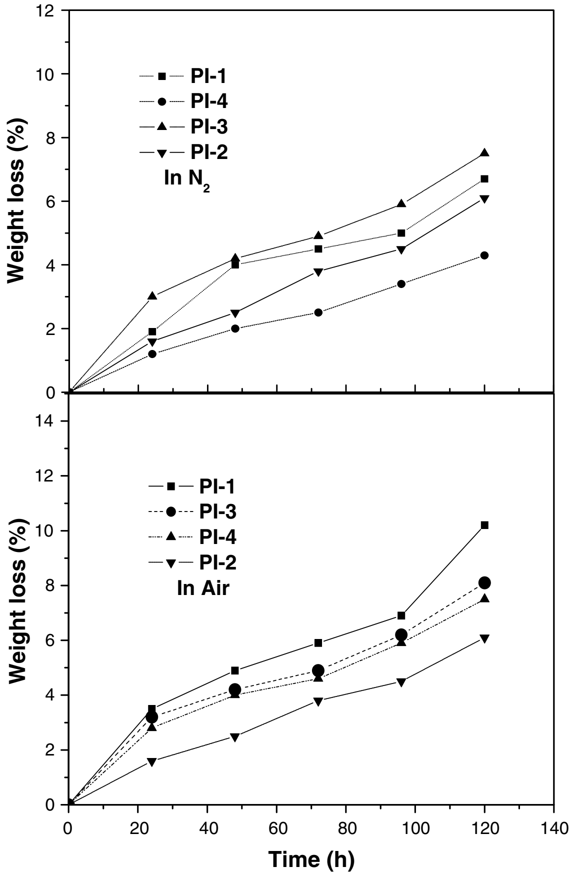


Fig. 6. Thermal and thermo-oxidative stability of the polyimides at 350 °C.

3.5. Mechanical properties

The fluorinated polyimide films were synthesized by casting the chemically imidized polyimide solutions in NMP on glass surface, followed by thermal baking in a schedule of 80 °C/1 h, 120 °C/1 h, 180 °C/2 h and 220 °C/2 h to remove the solvents. A non-fluorinated PI-5 was also prepared in a two-step thermal imidization as comparison. Table 4 outlined the tensile strength and modulus of the polyimides. The fluorinated polyimide films exhibited the tensile strength in the range of

Table 4
Mechanical properties of the polyimides

Polyimide	PI-1	PI-2	PI-3	PI-4	PI-5
Elongation at break (%)	9.5	10.3	10.8	11.0	24.1
Tensile strength (MPa)	105	87.6	78.1	117	123
Young modules (GPa)	1.12	0.85	0.72	0.63	1.50

78.1–117 MPa, elongation at breakage of 9.5–11% and Young modules of 0.63–1.12 GPa, respectively. PI-1 based on the aromatic dianhydride PMDA, exhibited low elongation at breakage of 9.5% due to the rigid polymer backbone. PI-4 derived from aromatic dianhydride ODPA possessed the best mechanical properties with the elongation at break of 11% and tensile strength of 117 MPa, individually, which was attributed to the flexible C–O–C chain in the structure. The non-fluorinated PI exhibited better mechanical properties than the fluorinated ones, which could be attributed to the higher molecular weight arising from the excellent reaction activity of ODA to PMDA.

3.6. Dielectric and insulating properties

Good dielectric and insulating properties are desirable for the application of polyimide on microelectronic industry such as microelectronic package [17–20]. As shown in Table 5, polyimides exhibited the dielectric constants ranged in 2.71–2.95 at 1 MHz, which was lower than the conventional PI-5 (3.25) or the well-known commercial polyimide Kapton® (3.40 at 1 MHz), and the dissipation factor ranged in $2.8–3.5 \times 10^{-3}$. Volume resistivity was measured from 1.90×10^{15} to 1.05×10^{16} Ω cm and surface resistivity from 1.23×10^{14} to 6.71×10^{14} Ω. The insulating voltage ranged in 92.0–122.6 kV/mm, which performed little change after boiling in water for 6 h. These excellent dielectric and insulating properties might be attributed to the incorporation of trifluoromethyl groups which possessed low electronic polarizability both in the main backbone and side chain of the polymer. Hence, PI-2 prepared from 6FDAM/6FDA indicated the best dielectric and insulating properties due to the highest loading of fluorine. PI-5 possessed a higher insulating voltage of 178 kV/mm than the fluorinated ones possibly owning to the good film formation.

The water adsorptions of polyimides were determined by immersing film in boiling water at 100 °C for 30 min, and then weighed to measure the weight adsorptions. The water adsorptions for the fluorinated polyimides ranged in 0.42–0.95%, in which PI-2 exhibited the lowest value of water adsorption of 0.42% due to the maximum fluorine content which prevented moisture adsorption on the surface of the polyimides. Note that the water adsorptions of fluorinated polyimides are much lower than that of non-fluorinated PI-5 (2.65%) attributed to the hydrophobicity of trifluoromethyl groups, implying the incorporation of fluorine-containing group into polyimides is an effective method to reduce the water adsorptions.

3.7. Optical properties

Table 5 also showed the UV–vis data of the fluorinated polyimide films with thickness of 25 um. The cut-off absorptions of the fluorinated polyimide films were 330 nm (PI-2), 340 nm (PI-4), 360 nm (PI-3) and 375 nm (PI-1), respectively, whereas the non-fluorinated PI-5 was red shifted to 420 nm.

Table 5
Dielectric and optical properties of the polyamides[a]

Polyimide	PI-1	PI-2	PI-3	PI-4	PI-5
Ds (kV/mm)	92.0	122.6	98.6	110.0	178
Ds* (kV/mm)	90.5	121.8	96.0	107.4	170
ρ_v (Ω cm)	9.8×10^{15}	1.05×10^{16}	1.9×10^{15}	7.8×10^{15}	9.2×10^{15}
ρ_s (Ω)	4.18×10^{14}	6.71×10^{14}	1.23×10^{14}	3.85×10^{14}	5.6×10^{14}
ε_r (1 MHz)	2.95	2.71	2. 91	2.89	3.25
$\tan\delta$	3.5×10^{-3}	2.8×10^{-3}	3.1×10^{-3}	2.9×10^{-3}	4.5×10^{-3}
λ_{cut} (nm)	375	330	360	340	420
T (at 400 nm)	5%	61%	18%	45%	0
W_u (%)	0.95	0.42	0.84	0.52	2.65

[a] Ds: dielectric strength; Ds*: dielectric strength after boiling in water for 6 h; ρ_v: volume resistivity; ε_r: dielectric constant at 1 MHz, 25 °C; ρ_s: surface resistivity; $\tan\delta$: dissipation factor; λ_{cut}: cutoff wavelength in UV–vis spectra. T: transparency of films at 400 nm; W_u: water adsorption.

Transparency (T%) of the fluorinated polyimide films at 400 nm decreased in the order of 61% (PI-2) > 45% (PI-4) > 18% (PI-3) > 5% (PI-1). PI-5 exhibited no transparency at 400 nm indicating a low optical property. PI-2 derived from 6FDAM and 6FDA exhibited the highest transparency with cut-off absorptions of 330 nm and transparency at 400 nm of 61%. Clearly, the fluorinated polyimides possessed improved optical properties as compared with the non-fluorinated PI-5, which might be attributed to the effect of electron-withdrawing C–F bond decreasing the formation of charge-transfer complex (CTC) between polymer chains.

4. Conclusions

A novel fluorinated diamine 6FDAM was synthesized and characterized, which was then employed to prepare a series of fluorinated polyimides with commercial aromatic dianhydrides. The fluorinated polyimides exhibited excellent solubility, low moisture adsorption of 0.42–0.95%, low dielectric constant of 2.71–2.95 at 1 MHz, high dielectric strength of 92.0–122.6 kV/mm and high optical transparency with cutoff wavelengths of UV–vis at 330–375 nm. The polyimides also indicated good mechanical properties, excellent thermal and thermo-oxidative stability. Compared to the non-fluorinated PI-5 (PMDA/ODA), the fluorinated polyimides possessed better solubility, lower dielectric constant and water adsorption as well as higher optical transparency, which showed good potentials in microelectronic applications as dielectric and insulating materials.

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